p-type conductivity and donor-acceptor pair emission in Cd1−xFexS dilute magnetic semiconductors

X. J. Wu, D. Z. Shen, Z. Z. Zhang, J. Y. Zhang, K. W. Liu et al.

Additional information on Appl. Phys. Lett.

p-type conductivity and donor-acceptor pair emission in Cd$_{1-x}$Fe$_x$S dilute magnetic semiconductors

X. J. Wu
Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

D. Z. Shen, Z. Z. Zhang, J. Y. Zhang,[a] K. W. Liu, B. H. Li, Y. M. Lu, D. X. Zhao, and B. Yao
Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

Cd$_{1-x}$Fe$_x$S thin films with different Fe contents were grown on *c*-plane sapphire by low-pressure metal organic chemical vapor deposition. The resistivity of the thin films was found to increase with the addition of more Fe contents into the Cd$_{1-x}$Fe$_x$S thin films by elevating the growth temperature, which was attributed to the ionization of holes from trivalent Fe ions. High density Fe doping eventually reversed the conductivity of Cd$_{1-x}$Fe$_x$S thin film from *n* to *p* type. With increasing Fe content, the band-to-band transition at 2.5 eV was suppressed while the emission from the donor-acceptor pairs at 2.0–2.4 eV finally dominated the photoluminescence spectra. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2425028]

In recent years, there has been increasing interest in epitaxial growth of semiconducting materials doped by transition metal ions, so-called dilute magnetic semiconductors (DMSs), such as MnGaAs, MnCdTe, CoZnO, and FeZnO.[1–4] DMSs offer the great opportunity to integrate the magnetic, electrical, and optical advantages into a single semiconductor material, which provides many potential applications in the field of semiconductor spintronic and optoelectronic devices. In addition to the introduced new functionalities, incorporation of transition metal ions was found, however, to inevitably bring side effects on the optical and electrical properties of semiconductors. It is well known that transition metal ions usually not only degrade the crystal quality of a semiconductor compound but also act as quenching centers for fluorescence.

Although many works on Fe-based DMS have been reported previously, the influences of doping on its electrical and optical characteristics are not well studied yet. In the present work, we report the dependences of the electrical conductivity and photoluminescence in Cd$_{1-x}$Fe$_x$S thin films on the Fe contents. With increasing doping density, we find that the conductivity of the Cd$_{1-x}$Fe$_x$S thin film shows an interesting conversion from *n* to *p* type, accompanied with significant enhancement of the donor-acceptor pair emission in the photoluminescence spectra.

Cd$_{1-x}$Fe$_x$S thin films were grown on *c*-plane sapphire by using low-pressure metal organic chemical vapor deposition (LP-MOCVD). High purity hydrogen was used as the carrier gas. The chamber pressure was kept at about 1×10^4 Pa during material growth. Samples A–D with different Fe contents were obtained by simply changing the growth temperature from 270 to 360 °C with a step of 30 °C. Sample E with Fe content up to 0.14 was grown at 330 °C by increasing the flow rate of Fe(CO)$_5$ source.

The crystal structure of Cd$_{1-x}$Fe$_x$S thin films was characterized by x-ray diffraction (XRD) using a rotating anode x-ray diffractometer with Cu Kα radiation at 0.154 nm. A Lake Shore 7707 Hall measurement system was employed to measure the electrical properties of the thin films. Photoluminescence (PL) measurements were performed on a JY-630 micro-Raman spectrometer in a backscattering geometry configuration. The excitation source for the PL is the 325 nm line of a He–Cd laser.

The Fe contents in samples A, B, C, D, and E are 0.0025, 0.0072, 0.0149, 0.0455, and 0.1400, respectively, which were measured by energy dispersive spectroscopy. The increase of Fe content with elevating growth temperature was attributed to the fact that the pyrolysis of Fe(CO)$_5$ was more efficient at high temperatures. Figure 1 shows the XRD patterns of the Cd$_{1-x}$Fe$_x$S samples. No other diffraction peaks were observed from the thin film except the peak around 26.6°. The diffraction peak of Cd$_{1-x}$Fe$_x$S shifts to larger angle with in-

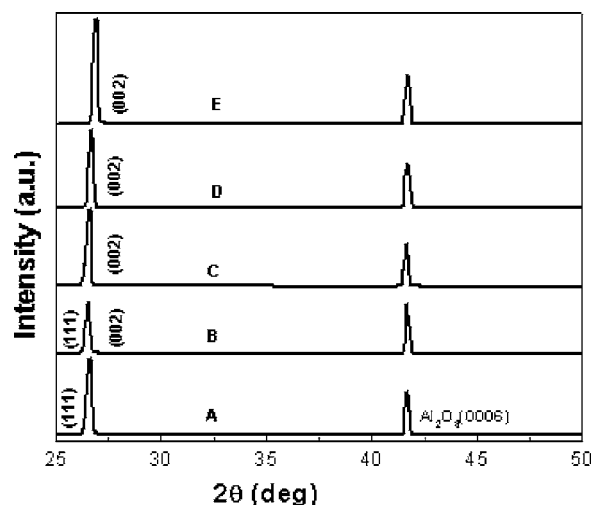FIG. 1. XRD patterns of the Cd$_{1-x}$Fe$_x$S samples. The peak at 41.68° is from (0006) diffraction of the sapphire substrates.

[a]Author to whom correspondence should be addressed; electronic mail: zhangjy53@yahoo.com.cn

89, 262118-1

TABLE I. Electrical properties of the samples with different Fe contents.

Fe content	Resistivity (Ω cm)	Type	Carrier concentration
0.0025	0.25	*n*	3.11×10^{18}
0.0072	0.81	*n*	1.98×10^{18}
0.0455	6.92	*n*	1.35×10^{17}
0.1400	239.7	*p*	3.81×10^{15}

creasing growth temperature, which agrees with more and more Fe ions with smaller radius (0.74 Å) replacing the Cd ions (0.96 Å) in the lattice. The unusual shift of the peak for the sample grown at temperature lower than 300 °C was caused by the phase reversion from cubic to hexagonal structure at 300 °C, which will be discussed elsewhere.[5]

Revealed by magnetism measurements at low temperatures, all the samples show Van Vleck-type paramagnetism,[5] which was reported previously in Fe-doped DMS. Most interestingly, we find that the Fe doping modifies the electrical and optical properties of the $Cd_{1-x}Fe_xS$ thin films significantly in addition to the magnetic properties.

Undoped CdS, either cubic or hexagonal phase, usually shows *n*-type conductivity because of the strong self-compensation caused by intrinsic defects. In our experiments, however, *p*-type conductivity was evidently observed in $Cd_{1-x}Fe_xS$ films with certain Fe doping level. Table I presents the electrical properties of $Cd_{1-x}Fe_xS$ films measured at room temperature. The $Cd_{1-x}Fe_xS$ film with $x = 0.0025$ shows *n*-type characteristics with carrier concentration of 3.1×10^{18} cm^{-3} and resistivity of 0.25 Ω cm. With increasing Fe content in the samples, the electron concentration decreases and the resistivity increases gradually. When x reaches 0.14, the conductivity reverses its sign from *n* type to *p* type with carrier concentration of 3.8×10^{15} cm^{-3} and resistivity of 239.7 Ω cm. As is well known, to obtain *p*-type conductivity for II-VI semiconductors, group I elements (such as copper) and group V elements [such as N (Ref. 6 and 7)] were usually employed as dopants for acceptors. It is surprising and interesting that a group VIII B element in CdS lattice plays an acceptor. In the x-ray photoelectron spectra of the films (not shown here),[5] signal from Fe^{3+} could be observed. The Fe^{3+}, formed by the oxidation of Fe^{2+} ion on the sample surface, can return to bivalent state by releasing a hole. Similar process was discussed in a previous report on NiO:Fe.[8] The mechanism can be depicted as follows:

$$Fe_{Cd}^{2+} + O_{2ad} = Fe_{Cd}^{3+} + O_{2ad}^-, \qquad (1)$$

$$Fe_{Cd}^{3+} = Fe_{Cd}^{2+} + h. \qquad (2)$$
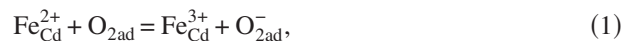
The subscript "ad" denotes that the O_2 molecule is adsorbed at the film surface, and subscript "Cd" denotes that the Fe atom is at the Cd site.

With increasing Fe content in the $Cd_{1-x}Fe_xS$ thin film, electrons from intrinsic defects were believed to be compensated gradually by holes. Once the hole concentration overcomes that of electrons, the reversion from *n*- to *p*-type conductivity will take place.

To study the influence of Fe doping on the optical properties of the $Cd_{1-x}Fe_xS$ films, PL spectra of samples A–D were measured at 92 K, as shown in Fig. 2. The intensity of the spectra was normalized for clarity. The PL spectra contain two parts, which are the band-to-band transition at about 2.5 eV (Ref. 9) and defect related emission located at
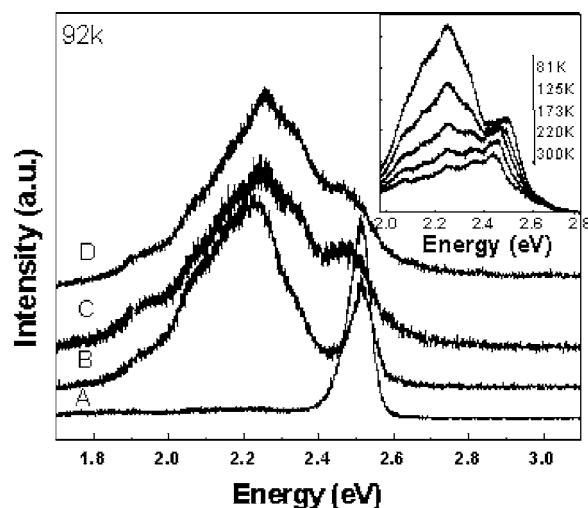

FIG. 2. PL spectra of samples A–D measured at 92 K. The inset is the PL spectra of sample C measured at various temperatures.

2.0–2.4 eV, respectively. The small humps superposed on the low-energy side of the defect emission are originated from interferences. With increasing Fe content, the band-to-band emission of the $Cd_{1-x}Fe_xS$ films is suppressed gradually and the defect related emission finally dominates the PL spectra, which is because the Fe ions usually play quenching centers for luminescence in semiconductors. Furthermore, we also find that the defect related emission band shifts to higher energy side with increasing Fe content. The PL spectra of sample C measured at various temperatures were shown in Fig. 2 as an inset. It is noted that the defect emission quenches with increasing temperature dramatically. We believe this emission is dominated by the donor-acceptor pair (DAP) transition, which is further supported by our following discussion, although Cd interstitial or Cd vacancy related emission at about 2.2 eV may also contribute to this band.[10]

Figure 3 shows the PL spectra of sample C at 92 K measured under optical excitations with various densities. With increasing excitation density, the higher energy side of the defect emission was enhanced more obviously compared to the low-energy side, which is a typical characteristic of DAP
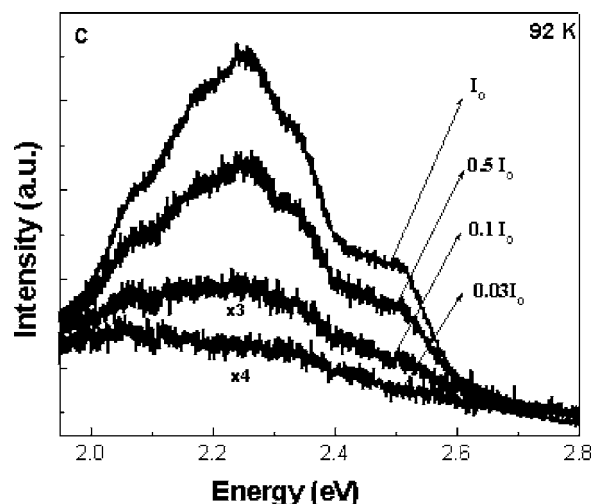

FIG. 3. PL spectra of sample C under various excitation densities at 92 K, where I_0 is 1 kW cm^{-2}.

emission. The acceptors in DAPs is attributed to trivalent Fe ions which can offer holes as mentioned above. With increasing Fe content, DAPs with closer distance is believed to appear with larger opportunity. This will lead to the increase of the emission at the higher energy side, which is in excellent agreement with the observed blueshift of the emission with increased Fe contents, as shown in Fig. 2. Donors of the DAPs could be from the interstitial Cd atoms or sulphur vacancies.

In summary, $Cd_{1-x}Fe_xS$ thin films with Fe contents from 0.0025 to 0.14 were grown on *c*-plane sapphire by LP-MOCVD. With increasing Fe content in the $Cd_{1-x}Fe_xS$ thin films, the conductivity of the films could possibly reverse from *n* to *p* type. This conductivity reversion was attributed to the holes generated from trivalent Fe ions close to the film surface, which were formed via oxidation by the O_2 adsorbed on the film surface. With increasing Fe content, DAP related emission band at 2.0–2.4 eV started to dominate the luminescence, while the band-to-band transition at 2.5 eV was suppressed gradually.

[1] G. M. Dalpian and Su-Huai Wei, Phys. Status Solidi B **243**, 2170 (2006).
[2] S. Mackowski, H. E. Jackson, and L. M. Smith, Appl. Phys. Lett. **83**, 3575 (2003).
[3] C. H. Park and D. J. Chadi, Phys. Rev. Lett. **94**, 127204 (2005).
[4] Jeong Hyun Shim, Taesoon Hwang, and Soonchil Lee, Appl. Phys. Lett. **86**, 082503 (2005).
[5] X. J. Wu, D. Z. Shen, Z. Z. Zhang, K. W. Liu, B. H. Li, J. Y. Zhang, Y. M. Lu, D. X. Zhao, B. Yao, X. G. Ren, and X. W. Fan, Solid State Commun. (in press).
[6] P. J. Sebastian, Appl. Phys. Lett. **62**, 2956 (1993).
[7] V elements such as N [Gene Strull, J. Appl. Phys. **24**, 1411 (1953)].
[8] Jianfei Wang, Jingnan Cai, Yuan-Hua Lin, and Ce-Wen Nan, Appl. Phys. Lett. **87**, 202501 (2005).
[9] G. Perna, V. Capozzi, M. Ambrico, V. Augelli, T. Ligonzo, A. Minafra, L. Schiavulli, and M. Pallara, Thin Solid Films **453**, 187 (2004).
[10] R. Lozada-Morales, O. Zelaya-Angel, and G. Torres-Delgado, Appl. Surf. Sci. **175**, 562 (2001).